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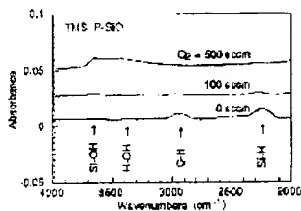
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## (54) FORMATION METHOD OF SILICON OXIDE FILM

(57) Abstract:

PURPOSE. To form a silicon oxide film which is small in an OH content group and excellent in moisture permeability preventing properties and coated with a high offset.

CONSTITUTION. A mixed gas of an oxidizing gas containing alkoxy silane and hydrogen is introduced, thereby forming a silicon oxide film having an Si-H bonding based on a plasma CVD method. This makes it possible to manufacture a semiconductor device having a high density and high reliability multilayer wiring at low cost.



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### 1. Technical Description of the Invention

[Industrial Application] this invention relates to the manufacture method of a silicon oxide and relates to the formation method by the CVD of the silicon oxide which insulates between the vertical wiring layers in the multilayer interconnection of a semiconductor device especially.

[Description of the Prior Art] In formation of the silicon oxide for semiconductor devices by CVD, the mono silane - SiH<sub>4</sub> has been used as a raw material from the former. However, in connection with the densification of a large-scale integrated circuit (LSI), the pattern size turned minute, it became the stage where now submicron processing was performed, and some trouble has arisen. For example, it is SiH<sub>4</sub> although the size of a wiring interval is becoming indispensable [ the embedding of the quality insulator layer to the portion into which the ratio (aspect ratio) of the depth (height of wiring) to between wiring exceeds 1 ] by submicron-one in the manufacture process of a multilayer interconnection. It is raised to such a detailed slot and the detailed level difference section of a high aspect ratio with the used CVD that sufficient insulator layer formation cannot be performed. Moreover, if it is going to dare apply, the problem of aluminum wiring being corroded and disconnected in permeation of the moisture from a portion in which the short circuit during wiring and covering nature were inferior will arise. Moreover, SiH<sub>4</sub> When oxygen (O<sub>2</sub>) and the nitrous oxide (N<sub>2</sub>O) of a oxidizing gas are contacted, it is also a problem that it reacts easily and is easy to generate particle. Moreover, SiH<sub>4</sub> It is self-ignition nature gas which will burn if ordinary temperature describes air, and when it mixes with \*\*\*\*\* gas, it is a dangerous material which has explosivity. This SiH<sub>4</sub> If in charge of use, employment which formed the facility in alignment with the regulations about a specific high pressure gas, and took care of safety enough must be performed, and the cost for it is also by no means cheap.

[0007] Above  $\text{SiH}_4(\text{g})$  In order to conquer the fault of the used plasma CVD method, a tetraethyl ortho silicate (henceforth, TEOS) is  $\text{SiH}_4$ . It has come to be used as a changing raw material. The silicon oxide formed by the plasma CVD method using TEOS is  $\text{SiH}_4$ . Excelling [ ] and [ ] the case where it uses in level difference covering nature, TEOS is a comparatively safe raw material, which self-ignition nature does not have, either.

19002 However, the silicon oxide formed by the plasma CVD method using TEOS has still left the problem by compactness, the transparent prevention property of moisture, and the content OH radical weight, SiH<sub>4</sub>. Compared with the silicon oxide which used as the source and was formed by the plasma CVD method, water resistance is inferior. Si-H combination hardly exists in a film, but this is considered because there are comparatively many OH bases. Moreover, polarity is large and a content OH basis enlarges the dielectric constant of a silicon oxide. Although OH basis can be reduced and a precise silicon oxide can be obtained if heat treatment of about 600-800 degrees C can be performed after film formation by the plasma CVD method using TEOS, since aluminum system wiring deteriorates, it is inapplicable. Furthermore, when it was going to form the fluid silicon oxide on the silicon oxide formed by the plasma CVD method using TEOS by the CVD which used an alkoxide and ozone, such as TEOS, there was a problem that a generation film from face served as the configuration where irregularity is intense, or the so-called ground denegency like dispersion in the thickness of a generation film becomes large because remarkable.

[Problems] to be Solved by the Invention] The purpose of this invention is to offer the formation method of the silicon oxide which was excellent in the flat nature which solves simultaneously the technical problem about the reduction or the removal, and the waterproof improvement in OH basis in a generation film, the technical problem of high rank difference covering, \*\*\*\* formation, and the technical problem that a ground dependency is abolished in film formation of silicon CVD.

[Means for Solving the Problem] The above-mentioned technical problem is Si source and O<sub>2</sub> so that oxidation gas, such as O<sub>2</sub> or N<sub>2</sub>O, and mixed gas may be introduced using the alkoxide which has Si-H combination as the Si source and the above HANSU ratio of Si-H/Si-OH in a generation film may become 1/3 or more. Or N<sub>2</sub>O is solvable with a means to set up flow rate and to form a silicon oxide by the plasma CVD method.

[function] The alkoxide which has Si-Hi combination is used for this invention as the Si source. This kind of alkoxide acts so that there may also be no self-ignition nature at the time of acting so that high rank difference covering nature may be secured as a property common to an alkoxide, and touching air, since it had Si-O combination in the interior of a molecule, process safety may

decreased by traps and bounds and the cost of a facility may be reduced, and it is  $\text{SiH}_4$ . It acts so that a main component and particle may also be reduced.

[0008] The  $\text{Si-H}$  combination included in  $\text{Si}$  source of this invention is incorporated also in a generation film by controlling oxidation gas to the flow rate of a proper field. Since the  $\text{Si-H}$  combination in this film works so that the trap of the moisture which is going to permeate may be carried out, it acts so that the transparency in the film of moisture may be prevented.  $\text{Si-H}$  combination which exists in a film front face works as an active site in which surface reaction occurs easily, and it acts so that the silicon oxide formation reaction in a front face may advance. On the other hand, a surface  $\text{Si-OH}$  combination has strong polarity, and it tends to be connected with a carbon compound with the oxygen which is a product in reactant gas, and after this carbon compound has reached the front face, it acts so that surface reaction cannot advance easily and may become. Therefore, in order to perform uniform and high-speed film generation, it is effective that the  $\text{Si-H}$  concentration in a front face is large, and it is larger. The density of  $\text{Si-OH}$  combination is small, i.e., a  $\text{Si-H/Si-OH}$  ratio. Since  $\text{H}$  and  $\text{OH}$  combines with most portions into which silicon combination of a silicon oxide was confused, when the  $\text{Si-H}$  combination in a film is made to increase,  $\text{Si-OH}$  concentration has the property of decreasing. And according to the experiment, 1/3 or more generation films act so that transparency of moisture may be prevented, and the abb sow BANSU ratio of  $\text{Si-H/Si-OH}$  acts this film so that a ground dependency may be abolished in the ozone CVD as an underlay film.

[0008]

[Example] The example of this invention is explained in detail using drawing. The structure of a plasma CVD room where it used for formation of a silicon oxide is shown in drawing 1. The case where trimethylsiloxane (TMS) is used for  $\text{Si}$  source is explained as an example. TMS was put into the container made from stainless steel, with the liquid source, carried out bubbling of the nitrogen gas which is a carrier gas, and introduced it into the CVD room. The temperature of the container of TMS set the flow rate of 25 degrees C and conveyance nitrogen gas to 0.2slm(s). In order that the gas coming from a container to a CVD room might suppress adsorption and liquefaction of gas, it attached the temperature gradient in 1 step at (60-100) degrees C. TMS and the mixed gas of  $\text{O}_2$  and  $\text{N}_2$  were put in from the gas introduction 1, the substrate 4 with a diameter of 4 inches was placed on the lower electrode 3, and RF power was impressed between the top electrode 2 and the lower electrode 3. The frequency of RF set 54kHz and RF power to 100W. In addition, the top electrode 2 and the lower electrode 3 could set up the position independently, respectively, and the electrode spacing here set them to 12mm. The CVD room is equipped with the infrared transparency aperture 7 for analyzing reactant gas.

[0009] Next, the infrared absorption spectrum at the time of introducing TMS and being referred to as pressure 4 Torr was shown in drawing 2. This gas is the composition shown in drawing 2, and contains  $\text{C-H}$ ,  $\text{Si-H}$ , and  $\text{Si-O}$ . Drawing 3 is the infrared absorption spectrum of the reactant gas of the plasma state which impressed RF (RF power) considering as the plasma state -- everything but introductory gas -- 1775cm-1 -- formaldehyde ( $\text{HCHO}$ ) --  $\text{H}_2\text{O}$  by which a  $\text{O}_2$  stuck to the 2360cm-1 neighborhood to the 3740cm-1 neighborhood, and  $\text{Si-OH}$  combination stuck to the silica to the 3400cm-1 neighborhood. Moreover, the 3600cm-1 neighborhood and the 1600cm-1 neighborhood -- molecule-like  $\text{H}_2\text{O}$  it accepts, although it is little.

[0010] Next, an example of the infrared absorption spectrum of the formed silicon oxide is shown in drawing 4. On the relation of a dilution in oxygen 100sec and 500sec(s), 0.95 \*\*\*\*\* of abb sow BANSU are set to 0.025, respectively, and it is shown. 1slm and oxygen set [ pressure 1Torr, 12mm of electrode spacing, and the conveyance nitrogen gas of TMS 0.2slm(s), the substrate temperature of 350 degrees C, and dilution nitrogen gas ] membranous formation conditions to C - 500sec,  $\text{H}_2\text{O}$  to which  $\text{Si-OH}$  of the 3660cm-1 neighborhood and the 3400cm-1 neighborhood stuck when oxygen was 500sec(s) it accepts and has become a spectrum configuration equivalent to the silicon oxide at the time of using TEOS as a raw material. When oxygen is 100sec(s), abb sow BANSU of  $\text{Si-OH}$  decreases, and  $\text{Si-H}$  is accepted in the 2200cm-1 neighborhood. When oxygen is set to 0sec(s), a film grows. At this time,  $\text{Si-OH}$  decreases to a very small value, and abb sow BANSU of  $\text{Si-H}$  and  $\text{C-H}$  becomes large. Per abb sow BANSU of drawing 4 and also the result which measured the oxygen flow rate dependency in detail were shown in drawing 5 here. OH basis-related abb sow BANSU increases with the increase in an oxygen flow rate, and  $\text{Si-H}$  and  $\text{C-H}$  decrease with the increase in an oxygen flow rate. By changing the flow rate of TMS and oxygen, it was confirmed that the amount of the  $\text{Si-H}$  combination in the silicon oxide to generate or OH basis is changeable.

[0011] Next, oxidant (TES) is in the material to which TMS and the property were similar. Although the same oxygen flow rate dependency as the case of TMS was shown when TES was used as  $\text{Si}$  source, when the same flow rate compared, the result that abb sow BANSU of  $\text{C-H}$  in a film was large 20 to 50% was brought.

[0012] Next, in order to evaluate the level difference section covering configuration at the time of using TMS, the cross section of the conditions from which the silicon oxide of a flat part is set to 300nm using a sample with a slot with a width of face [ of 350nm and a depth of 600nm was observed by SEM. Judging from the state of the overlying of a level difference edge, when TMS is used as  $\text{Si}$  source, a configuration almost equivalent to the case where TEOS is used is acquired, and it is  $\text{SiH}_4$ . It turns out that the configuration at the time of using is excellent.

[0013] Next, the oxygen flow rate dependency of the refractive index n of a generation film was shown in drawing 6. Although it is a value equivalent to the silicon oxide which used TEOS as the raw material when an oxygen flow rate is large, if an oxygen flow rate is decreased, a refractive index will increase. When an oxygen flow rate is 20 or less sec(s), the increase in a refractive index is remarkable.

[0014] 5% of next, concentration The result which measured the etch rate of a silicon oxide with dilution HF liquid was shown in drawing 7. Since it is usually 10 - 12 nm/min, the silicon oxides formed by the plasma CVD method which used as the raw material TEOS currently generally used for the multilayer interconnection of LSI are 2.5 nm/min of a thermal oxidation film. It is



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#### DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Explanatory drawing of a plasma CVD oven.

[Drawing 2] The infrared-absorption-spectrum view of TMS gas.

[Drawing 3] The infrared-absorption-spectrum view of the reactant gas in plasma CVD.

[Drawing 4] The infrared-absorption-spectrum view of the silicon oxide of this invention.

[Drawing 5] O2 of absorption BANDS of the molecular binding in a silicon oxide Property view showing a flow rate dependency.

[Drawing 6] O2 of a refractive index Property view showing a flow rate dependency.

[Drawing 7] The property view showing O2 flow-rate dependency of the etch rate by 0.5% fluorine acid solution.

[Drawing 8] The property view showing O2 flow-rate dependency of the field granularity of TEOS-O3 film formed on the silicon oxide of this invention.

[Description of Notations]

1 / -- A lower electrode, 4 / -- A substrate, 5 / -- RF electrode, 6 / -- The wall of a CVD oven, 7 / -- The aperture for infrared observation, 8 / -- Reactant gas exhaust port, 1 / -- Gas introduction piping, 2 / -- An up electrode, 3

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## CLAIMS

Changed

[Claim 1] The formation method of the silicon oxide characterized by forming the silicon oxide which is mixed with the source of oxygen and contains Si-H combination by the plasma CVD method by making into the source of silicon the alkoxide which has Si-H combination.

[Claim 1] The formation method of a silicon oxide that the maximum of absorption of Si-H of the range of 2100cm<sup>-1</sup> in the infrared absorption of a generation film (on claim 1 publication and ) to 2490cm<sup>-1</sup> is 1/3 or more of the maximum of absorption of Si-CH<sub>3</sub> of the range of 3700cm<sup>-1</sup> to 3800cm<sup>-1</sup>.

[Claim 3] The formation method of a silicon oxide that the aforementioned source of silicon is trimethoxysilane in claims 1 or 2

(Claim 4) The formation method of a silicon oxide film which forms a silicon oxide by using the aforementioned silicon oxide as an underlayer in claims 1, 2, or 3.

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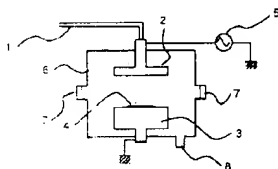
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## DRAWINGS

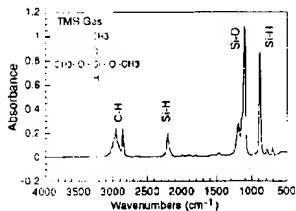
[Drawing 1]

FIG. 1



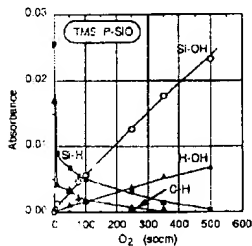
[Drawing 2]

FIG. 2



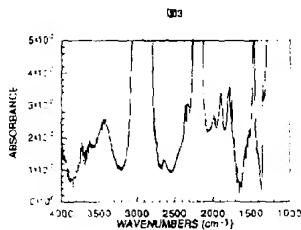
[Drawing 3]

FIG. 3

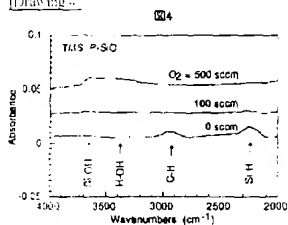


[Drawing 4]

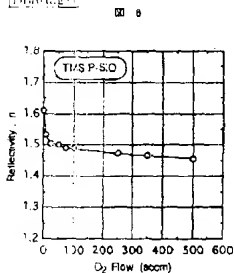




[[Drawing 1]]



[[Drawing 2]]



[[Drawing 3]]

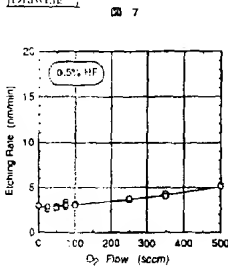
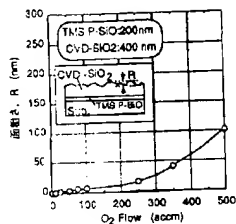


Figure 2

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